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SYNTHESIS OF TINTED GLAZE COATINGS BASED ON METADIABASE

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The synthesis of tinted pigment-free low-melting glazes based on Belarus metadiabase is investigated. The time/temperature parameters for formation of high-quality glaze coatings are identified. The processes of structure and texture formation in the coatings are studied in relation to the chemical composition of the glass and the character of crystal-phase formation, and their main properties are evaluated.

Tinted glazes are widely used in the ceramics industry to decorate facing tiles, majolica, and other products. Expensive colorants and pigments are mostly used to impart the required color to such glazes.

Previously conducted integrated research on metadiabase, which is a magma rock of basic composition [1, 2], indicated the possibility of using these rocks in production of tinted glazes without additional pigments, which permits expansion of natural resources in ceramic production and reduction of the consumption of expensive and scarce pigments.

The purpose of the present study was to synthesize tinted pigment-free low-melting glazes for ceramic products that are based on metadiabase, to establish the general regularities of formation of the color and texture of the coatings, and to assess their main properties and structure in relation to the nature of the formation of crystal phases under various heat-treatment parameters.

The initial system selected for synthesis of fritted glaze coatings was $R_2O - RO - Fe_2O_3(FeO) - B_2O_3 - Al_2O_3 - SiO_2$ (where $R_2O = Na_2O + K_2O$, $RO = CaO + MgO$). The content of basic oxides in the glaze composition was varied within the following limits (here and elsewhere in wt.%): 28.25 – 59.84 SiO_2 , 4.42 – 8.28 ($Fe_2O_3 + FeO$), 5.00 – 40.00 B_2O_3 . Most of the amount of the oxides comprising the investigated system was introduced with metadiabase, whose content was varied from 45 to 75%. The missing part of SiO_2 was furnished by quartz sand, of Na_2O by soda ash, and of B_2O_3 by boric acid. The modification of initial system 1 consisted in replacement of 5% B_2O_3 with 5% CaO and an increase in the Na_2O content by 2.5% (system 2). In this way, variations of the sum ($R_2O + RO$) and the ratio $R_2O : RO$ were provided. These values for system 1 were equal to 15.6 – 21.0% and 1.2 – 1.7%, respectively, and for system 2 were equal to 23.1 – 28.4% and 0.95 – 1.20%, respectively.

The glaze glasses were melted in porcelain crucibles of 0.3-liter capacity in a gas flame furnace at a temperature of 1350 – 1400°C with a 1.5-h hold at the maximum temperature until a homogeneous glass melt was obtained, which exhibited no visible inclusions in a filament test. The glasses had a homogeneous degree of melting, good melting and working properties, a black-green color, clarity, and an x-ray-amorphous state. An analysis of all the glasses using the electron microscopy method established the existence of phase separation in the form of developed fine-drop liquation. The drop size was 0.2 – 0.3 μm .

A study of the crystallization properties of solid samples of glaze glass demonstrated that volume crystallization of the glass does not take place in the temperature interval of 600 – 1000°C, only opalescence is typically observed, and a surface crystallization film is formed, which mostly consists of spinels: $MgFe_2O_4$ and $FeFe_2O_4$. It should be noted that opalescence is typical of compositions in which the B_2O_3 content exceeds 25%.

According to DTA data, softening of the glass takes place within the temperature interval of 515 – 570°C, and an exothermic effect presumably related to the crystallization process is registered at 830 – 900°C.

Based on a study of the main physicochemical properties of the glaze glasses, it is established that the density of the glass depends on its chemical composition, and for systems 1 and 2, it varies within the intervals of 2430 – 2620 and 2520 – 2720 kg/m^3 , respectively. The microhardness of the glasses was measured on a PMT-3 microhardness meter using the method of diamond pyramid indentation into the glass surface. The microhardness of the glaze glasses of the systems considered depends on the glass composition and varies in the range of 5790 – 7460 MPa. An increase in the B_2O_3 content decreases the microhardness, due to conversion of a major portion of the boron ions to three coordination, after which these ions form their own structure that degrades

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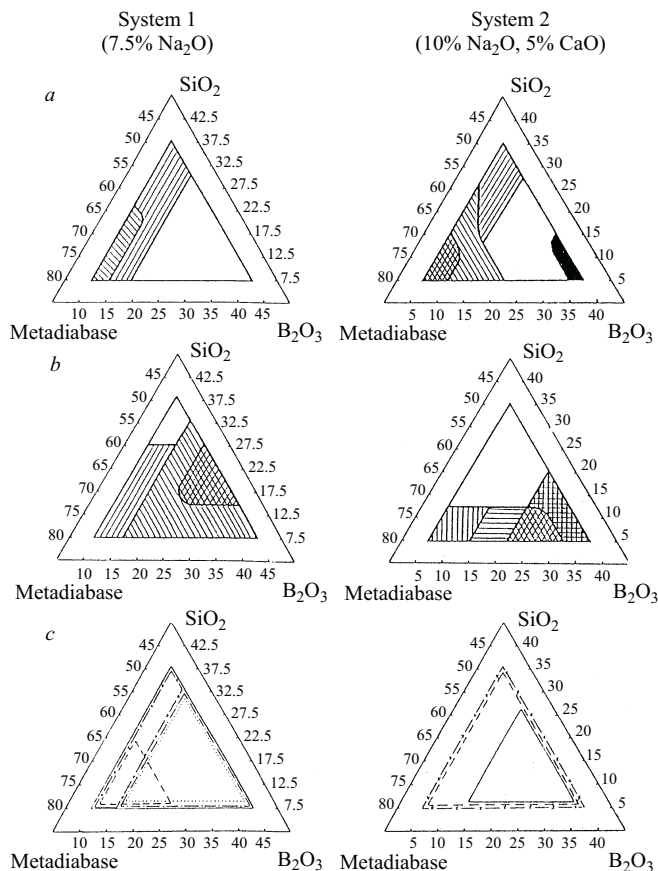


Fig. 1. Texture (a), color (b), and phase composition (c) of glaze coatings based on metadiabase in the case of a fusion temperature of 900°C and a hold of 15 min. Coating texture: stony, dull; dull; semidull; lustrous; overburned. Coating color: green; yellow-green; brownish-yellow; dark green; cherry; red-brown; dark brown. Phase composition: —) hematite, -x-x-) diopside phase, ---) oligoclase, - · - · -) maghemite,) sodium-magnesium silicate.

the strength and chemical properties of the glasses, since the asymmetric [BO₃] triangles have very weak bonds between each other. With an increasing SiO₂ content, the microhardness of the glass increases, since silicon oxide has a high degree of bond covalence and increases the strength of the glass structure.

A study of the quality of the glaze coating versus the temperature/time firing conditions was carried out for heat treatment of glaze suspensions of 50–55% moisture content deposited on a ceramic substrate with subsequent air drying and firing in an electric furnace. The heat treatment was carried out at a temperature of 750–950°C with an interval of 50°C and a hold for 15 min and 1 h at the maximum temperature. The temperature rise to the maximum level lasted 1 h with subsequent natural cooling in a closed furnace.

Experiments indicated that spreading and vitrification of the coatings are absent up to 680°C, and only coalescence of the glaze layer to the ceramic substrate takes place.

Formation of high-quality glaze coatings in the systems considered is observed in the temperature interval of 850–950°C, while the coating texture varies from lustrous (luster 60–73%) to semidull and dull (luster 43–55 and below 35%, respectively). The color range of the glaze coatings assessed visually in accordance with the scale in a 1000-color atlas prepared by the D. I. Mendelev All-Russia Research Institute is represented by various color shades, from yellow-green to red-brown and cherry. The optimum firing temperature is 900°C. It is established that a high-quality coating is achieved with a 15-min hold, and when the hold is extended to 1 h a slight improvement in quality is observed in certain coatings, which exhibit improved spreadability and a 2–3% increase in luster.

System 1 heat-treated at 850°C produces high-quality lustrous coatings for a B₂O₃ content exceeding 20%. If the B₂O₃ content is below 20%, dull and semidull areas are formed in the coating, which is due to the lower spreadability of such compositions. In system 2 the region of formation of lustrous coatings for the specified temperature is insignificant and is limited to a B₂O₃ content over 25% and a metadiabase content below 50%. Furthermore, a range of coatings with a stony dull texture is distinguished in system 2.

For a temperature of 850°C, the color of coatings of system 1 varies from red-brown (dull and semidull coatings) to dark brown (lustrous coatings), except for the region limited to an SiO₂ content over 30% and a B₂O₃ content below 15%, in which semidull green coatings are formed. The color variations in system 2 are more complicated. Thus, with an SiO₂ content over 15%, the coating color varies from brownish-yellow and yellow-green to green, and with a B₂O₃ content over 22.5% it changes to dark brown, which is related to formation of crystalline phases in firing.

Figure 1 represents regions of formation of texture, color, and phase composition in the considered systems for the optimum firing temperature of 900°C and a 15-min hold.

In system 1, with the temperature increased to 900°C, the type of coatings formed is modified. Thus, the regions of dull and semidull coating texture become smaller, while the region of lustrous coatings increases and for the specified temperature is limited to a content of B₂O₃ exceeding 17.5%. An increase in temperature causes a modification of the color characteristics: the glaze color is intensified and, as a consequence, the region of dark brown coatings expands. Furthermore, for the specified temperature, a cherry-colored glaze region is distinguished that is limited to a B₂O₃ content of 20.0–35.0% and an SiO₂ content of 15.0–27.5%. The green color range for 900°C is limited to a B₂O₃ content below 15% and an SiO₂ content over 27.5%. A further increase in the temperature to 950°C fosters intensification of the brown color and expansion of the lustrous-coating region.

In system 2 a similar increase in the temperature leads to the prevalence of green-colored coatings and a color modification from dark brown to cherry shades. The temperature increase facilitates the spreadability of the glaze and, accordingly, expansion of the lustrous-coating region, which for

900°C is limited to 12.5% B_2O_3 and less than 60% metadiabase. For the specified temperature, a yellow-green region with a stony texture is distinguished among the dull coatings. In the region of compositions limited to a metadiabase content below 47.5% and a B_2O_3 content equal to 25–35%, the glaze is overburned, and the coatings acquire blackish-green shades. With the temperature increased to 950°C, the region of glaze blistering is expanded and is limited to a B_2O_3 content over 20%. Black shades prevail in the blistering region. Moreover, the increase in temperature causes intensification of the green color and leads to expansion of the lustrous-coating region.

Thus, the studies preformed made it possible to identify regions of formation of glaze coatings of various textures and tints. The formation of a coating texture is determined by the chemical composition of the glass and by the glaze fusion temperature, whose increase decreases the viscosity and improves the spreadability. The color formation is more complicated and, apart from the listed factors, is also determined by the character of the emergence of crystal phases.

According to data of an x-ray phase analysis, crystallization processes start at a temperature around 750°C. In glazes of system 1 containing over 15% B_2O_3 in the glaze glass composition, the ferrous phase of maghemite $\gamma\text{-Fe}_2O_3$ and sodium-magnesium silicate Na_2MgSiO_4 are crystallized at 750°C, and the amount of the latter increases up to 900°C with subsequent melting. Maghemite is formed in a small quantity, and the temperature interval of existence of this phase is 750–900°C. Starting with 800°C, hematite $\alpha\text{-Fe}_2O_3$ is formed, and its maximum formation correlates with 900–950°C. Crystallization in compositions containing less than 15% B_2O_3 starts with formation of hematite, whose quantity increases with increasing temperature as well. Next, a diopside-like phase emerges at 800°C, whose compositions correlates with fassaite $Ca(Mg_{0.42}Fe_{0.31}Al_{0.28})(Si_{1.46}Al_{0.54})O_6$. As the content of SiO_2 in the composition grows, the diopside-like phase become the dominant one, which leads to formation of a green coating in the region limited to a SiO_2 content over 27.5% and a B_2O_3 content below 15%. Furthermore, with the metadiabase content in the glaze glass exceeding 60%, a plagioclase phase in the form of oligoclase is formed in the range of dull coatings, whose maximum correlates with 800–900°C. The composition of the crystallized oligoclase ranges from $0.7NaAlSi_2O_8 \cdot 0.3CaAl_2Si_2O_8$ to $0.83NaAlSi_2O_8 \cdot 0.16CaAl_2Si_2O_8$.

Thus, at the optimum firing temperature of 900°C, all compositions of system 1 contain hematite. With a B_2O_3 content over 15%, the compositions, in addition to hematite, contain maghemite and sodium-magnesium silicate. Compositions having less than 15% B_2O_3 contain fassaite. It is the crystallization of ferric phases that determines the formation of brown-colored coatings. When the glaze glass contains over 60% metadiabase, its phase composition is represented by oligoclase.

The phase composition of system 2 at a temperature of 900°C is represented by the diopside-like phase, oligoclase, and hematite, the diopside-like phase and oligoclase being present in all compositions of the system considered. Due to the increased content of CaO , which provides for formation of the diopside-like phase, this phase is the prevalent one, which determines the predominance of green color in this system. With a B_2O_3 content exceeding 12.5%, hematite is present as well. The hematite formation region virtually coincides with the region of lustrous-coating formation, and the amount of hematite formed is insignificant, except for the range of red-brown coatings, in which hematite is the prevalent phase.

The crystallization processes in system 2 start at a temperature of 750°C with formation of helenite $Ca_2Al[SiAlO_7]$, which is a compound with individual $[Si_2O_7]$ groups. Next, intense formation of plagioclase, whose composition is enriched in the anorthite component, and a diopside-type phase of the composition $Ca(Mg, Fe, Al)(Si, Al)_2O_6$ is observed. The plagioclase phase exists up to the temperature 900°C. Hematite is formed in a small quantity at a temperature above 900°C. The maximum formation of the diopside-type phase correlates with the temperature interval of 800–950°C. As the temperature grows, the crystalline phase dissolves, and the x-ray patterns at 980–1000°C exhibit only traces of the diopside-like phase. The crystallization of the primary intermediate phase, which is helenite, is presumably determined by the kinetic obstacles arising in the path of the crystallization of anorthite, due to the different energy of the crystal lattices, which is lower in helenite than in anorthite [3]. The primary crystallization of helenite correlates with the smaller share of oxygen in the energy of its crystal lattice than in the energy of the crystal lattice of anorthite, since this share increases in going from silicates with single tetrahedron groups (helenite) to silicates with the chain (diopside) and skeleton (anorthite) structures.

A comparative analysis of the chemical composition of the synthesized glazes and data of an x-ray phase analysis indicated that formation of the plagioclase phase is observed when the content of $(RO + R_2O)$ is over 18% and the ratio $R_2O : RO$ is below 1.4. The formation of hematite, maghemite, diopside, and sodium-magnesium silicate is determined by the ratio $(RO + R_2O) : (B_2O_3 + Al_2O_3 + Fe_2O_3)$. When this ratio is less than 0.5, the diopside-like phase is crystallized, and with this ratio exceeding 0.5, maghemite and sodium-magnesium silicate are formed. Hematite is crystallized when the ratio exceeds 0.8.

Thus, formation of the diopside-type phase and oligoclase in the glazes leads to formation of dull and semidull coatings and causes yellow-green tinting. Crystallization of hematite leads to brown shade tinting and results in the formation of coatings with heightened luster.

Electron microscope studies of green-yellow coatings identified crystallization of the diopside-like phase and oligoclase in the form of tabular prismatic crystals whose

size ranges from 0.3 to 0.7 μm . Hematite is formed in red-brown coatings in the form of hexagonal plates ranging from 0.2 to 0.4 μm .

Studies of the main physicochemical parameters of the coatings indicated that the TCLE of the glazes depends on the chemical composition of the glass and varies in the intervals $(57 - 72) \times 10^{-7}$ and $(62 - 83) \times 10^{-7} \text{ K}^{-1}$ for systems 1 and 2, the lustrous coatings having the lowest TCLE values. The microhardness of the glazes of the systems considered varies within the interval of 5730 – 6760 MPa.

The color characteristics of the glaze coatings were determined on an SF-18 spectrophotometer. The spectral parameters of the synthesized coatings were obtained. Their subsequent processing according to the method in [4] by calculating the coordinates X and Y of the color triangle (MKO color plot) indicated that the dominant wavelength (color tone) for coatings of the brown range is within the limits of 588 – 594 nm, and the tone purity (saturation) is 38 – 52%, while for green-color coatings these values are 580 – 584 nm and 43 – 62%, respectively.

The studies performed made it possible to determine the general regularities of the formation mechanism of the color and texture in tinted pigment-free glazes based on meta-

diabase in relation to the crystal-phase formation under different heat-treatment parameters. The results of the study point to the expediency of using metadiabase in synthesis of tinted pigment-free glazes and the possibility of producing high-quality glaze coatings based on them, with various textures from lustrous to dull and various colors from yellow-green to red-brown, which can be used for decoration of facing ceramics and majolica products.

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